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Process for the manufacture of composite materials and composite materials obtained by said process

This invention relates to the manufacture of composite materials comprising a matrix of set inorganic binder and fibre reinforcement.

Composite materials comprising a set inorganic binder (e.g. Portland cement) and fibre reinforcement (such as glass fibres), especially in the form of sheet or pipe, are commonly made by a process in which an aqueous slurry containing water-settable inorganic binder, reinforcing fibres (other than asbestos fibres, which for health reasons are no longer used) and web-forming fibres is dewatered, and the binder in the dewatered slurry is subsequently set, sometimes simply by being allowed to stand, sometimes by autoclaving or other moderate heating procedure. The web-forming fibre (usually cellulosic fibre) present in the slurry facilitates formation of a web in whatever plant (e.g. Hatschek, Magnani or Fourdrinier machine, or a simple press) is to be used to convert the binder and reinforcing fibres into the shaped state. The slurry, at least half of whose solids content is ordinarily formed by the water-settable inorganic binder, may also contain additional ingredients, such as perlite to modify the density of the composite material, exfoliated vermiculite to maintain its integrity in an outbreak of fire, or flocculant (e.g. polyacrylamide or other polyelectrolyte) in very small amount (e.g. 0.1% by weight) to improve drainage of water from the web and improve retention of fine particulate raw material in it.

By use of the process as just outlined for making composite material comprising a matrix of set inorganic binder and reinforcing fibres, it is often found that, during the later stages of setting of the binder, the composite material shrinks, and this very often leads to warping.

We have now found that by including a ball clay in the slurry that is dewatered, in an amount forming from 5 to 30% by weight of slurry solids and by employing low modulus carbon fibre as the reinforcing fibre, asbestos-free composite material can be obtained with improved properties in particular a reduced tendency to shrink and crack. A preferred range of ball clay content is 5—25% by weight, and 10—20% is particularly preferred.

Ball clay is a fine-grained, highly plastic, mainly kaolinitic sedimentary clay (The terms 'kalolinitic' and 'kaolinite' are mineralogical ones, indicating chemical composition and chemical structure; they are not to be confused with the term 'kaolin', used to denote a highly refractory clay which approaches the mineral kaolinite in chemical composition and structure but which — by contrast with ball clay — is hardly plastic at all.) Various types of ball clay have varying proportions of kaolinite, micaceous material, and quartz, with small amounts of organic matter and other minerals. Ball clays are used mainly in the manufacture of pottery and refractories — not by themselves, for they show excessive shrinkage, which may be as high as 20% when fired, but in admixture with other clays (such as the kaolin mentioned earlier) to impart plasticity to them and to increase the green strength of the unfired ware. The plasticity of ball clays, for which they are valued, is probably due to a combination of fine particle size and the presence of colloidal carbonaceous matter such as the so-called humic acids.

The invention can be applied to the manufacture of composite materials from any of the conventional water-settable inorganic binders. Thus, besides ordinary Portland cement, there may be used high alumina cements, slag cements and calcium binders. The carbon fibres used are those having a low Young's modulus (tensile modulus), not greater than 125 × 10^9Pascals. Carbon fibres of modulus in the range 10—100 GPa, and particularly 15—80 GPa, are specially preferred. We have found that low modulus carbon fibres are very readily dispersible in an aqueous suspension of water-settable inorganic binder, web-forming fibres and ball clay, and this ready dispersibility is in turn reflected in improved properties, especially reduced cracking, in the eventual composite material. Carbon fibres is preferably employed in an amount forming 0.1 to 2.5% by weight of the solids of the slurry, and in fibres length up to 100mm, preferably 3 to 50mm, with the range 4—10mm being particularly preferred. Carbon filament diameter may, for example, be 10—25μm.

The web-forming fibre employed is suitably cellulose, particularly that in cellulose pulp having a degree of freeness 50—95 on the Schopper Reigler scale; alternatively a so-called synthetic pulp of polyolefin (polypropylene or polyethylene), particularly having a degree of freeness 5 to 40° Schopper Reigler, may be used. Web-forming fibre will ordinarily form from 0.5 to 5% by weight of slurry solids.

The invention will now be further described with reference to the accompanying drawing, which is a diagram of a conventional Hatschek machine set up for sheet manufacture. The machine has troughs 1 and 2 in each of which a constant level 3 of aqueous slurry is maintained by controlled delivery of (a) more concentrated slurry from an associated reservoir (not shown) equipped with agitators to keep solids in suspension, and (b) dilution water to maintain the total solids content of the slurry in each trough at a suitable level, say 5% by weight. In the troughs themselves, the solids are kept suspended in the aqueous medium by paddles 4. Mounted in each trough is a rotary sieve 5, against which an endless conveyor felt 6 (which in the drawing rotates anti-clockwise) can be pressed by couch rollers 7 & 8 in response to

pressure from actuators 9 and 10 respectively, so that solids taken up from each trough onto its associated rotary sieve can be formed into a layer on the felt 6. The layer thus formed is de-watered as the free-draining felt moves on, de-watering being substantially completed as the felt passes over vacuum boxes 11 and 12. The layer of de-watered slurry is transferred from the felt 6 to the forming roll or 'bowl' 13 by press roller 14. When a thickness appropriate for the desired product has been built up on bowl 13, the material is slit axially (in response to a signal from control system 15 which counts the number of revolutions of the bowl) and removed from the bowl as sheet, and the water-hardenable binder component of it is allowed to set at ambient temperature or is set by autoclaving or other moderate heating of the material.

In applying the invention to the manufacture of composite material which includes low-modulus carbon fibre as reinforcing fibre, the troughs 1 and 2 are for example kept filled with aqueous slurry (solids:water = 1:25 by weight) made by adding to water at 45°C the following ingredients in the following proportions by weight.

Carbon fibre (length, 10mm; average diameter, 13 μm; average Young's modulus, 25GPa)	1.4%
Ordinary Portland cement	80.6%
Wood pulp (Schopper Reigler 55)	3.0%
Ball clay (bulk density 900 kg/m^3; predominant particle size less than 1μm)	15.0%

If for example a composite sheet material of thickness about 6mm is required, then with the conveyor felt rotating anti-clockwise in the drawing, rolls 7 & 8 are actuated to bring about deposition of slurry material from the slurry in troughs 1 and 2 onto the conveyor felt, and the formation on bowl 13 of a de-watered layer of slurry containing carbon fibre, Portland cement, cellulose fibre and ball clay. Build-up is continued until a de-watered slurry layer 6mm thick has been formed. Rolls 7 & 8 are then deactuated, and the material on bowl 13 is slit, stripped from the bowl, laid flat to form sheet, moulded to a desired (e.g. corrugated) form, and then set by being allowed to stand for 12 hours to form set composite material of acceptable flexural strength and impact strength. During setting of the Portland cement ingredient of the de-watered slurry, there was during a typical run practically no linear shrinkage (less than 0.25%) and no visible cracking of the shaped material.

A slurry formulation which is particularly effective for hand moulded goods where a very high degree of plasticity in the de-watered sheet is required is as follows:—

Low-modulus carbon fibre (length 5mm)	1.5%
Ordinary Portland cement	69.5%
Wood pulp	4.0%
Ball clay	25.0%

A slurry formation which is particularly useful for the production of pipes to convey potable water is as follows:—

Low-modulus carbon fibre (length 10mm)	1.4%
Ordinary Portland cement	80.6%
Wood pulp	2.0%
Synthetic Pulp (Solvay's polyethylene Pulpex)	1.0%
Ball clay	15.0%

This formulation has a reduced content of cellulose (bio-degradable material)

Claims

1. A process for the manufacture of an asbestos-free composite material comprising a matrix of set inorganic binder and fibrous reinforcement, by dewatering an aqueous slurry containing
(a) water-settable inorganic binder in an amount forming at least half of the solids content of the slurry,
(b) web-forming fibres selected from cellulose, polyethylene and polypropylene fibres,
(c) reinforcing carbon fibres, and
(d) a clay
and subsequently setting the binder in the de-watered slurry, characterised in that the clay employed is ball clay, which forms from 5 to 30% by weight of the solids content of the slurry and reduces shrinkage of the composite material during setting of the binder; and the carbon fibres are of tensile modulus not greater than 125 GPa, and form from 0.1 to 2.5% by weight of the solids content of the slurry.

2. A process according to claim 1, in which ball clay forms 10—20% by weight of slurry solids.

3. A process according to claim 1 or 2, in which the carbon fibre is of tensile modulus in the range 10—100 GPa.

4. A process according to claim 1 or 2, in which the carbon fibre is of tensile modulus in the range 15—80 GPa.

5. Composite material obtained by the process of any preceding claim.

Revendications

1. Procédé pour la fabrication d'un matériau composte exempt d'amiante comprenant une matrice de liant inorganique qui a fait prise et un renforcement en fibres par égouttage d'une bouillie aqueuse contenant:

(a) un liant inorganique hydraulique en une quantité formant au moins la moitié de la teneur en solides de la bouillie,

(b) des fibres formant nappe choisies entre les fibres de cellulose, de polyéthylène et de polypropylène,

(c) des fibres de carbone de renforcement, et

(d) une argile

et ensuite par prise du liant dans la bouillie égouttée, caractérisé en ce que l'argile utilisée est une argile figuline qui forme 5 à 30% en poids de la teneur en solides de la bouillie et réduit le retrait du matériau composite pendant la prise du liant, et les fibres de carbone ont un module de traction n'excédant pas 125 GPa et forment 0,1 à 2,5% en poids de la teneur en solides de la bouillie.

2. Procédé suivant la revendication 1, dans lequel l'argile figuline forme 10—20% en poids des solides de la bouillie.

3. Procédé suivant la revendication 1 ou 2, dans lequel les fibres de carbone ont un module de traction de l'intervalle de 10—100 GPa.

4. Procédé suivant la revendication 1 ou 2, dans lequel les fibres de carbone ont un module de traction de l'intervalle de 15—80 GPa.

5. Matériau composite obtenu par le procédé suivant l'une quelconque des revendications précédentes.

Patentansprüche

1. Verfahren zur Herstellung eines asbestfreien Verbundmaterials aus einer Matrix aus einem verfestigten anorganischen Bindemittel und einer faserartigen Verstärkung durch Entwässern einer wäßrigen Aufschlämmung, die

a) ein in Wasser verfestigbares anorganisches Bindemittel in einer Menge aufweist, die wenigstens die Hälfte des Feststoffgehaltes der Aufschlämmung darstellt,

b) bahnbildende Fasern, ausgewählt aus Cellulose-, Polyethylen- und Polypropylenfasern,

c) verstärkende Kohlefasern, und

d) einen Ton enthält, und

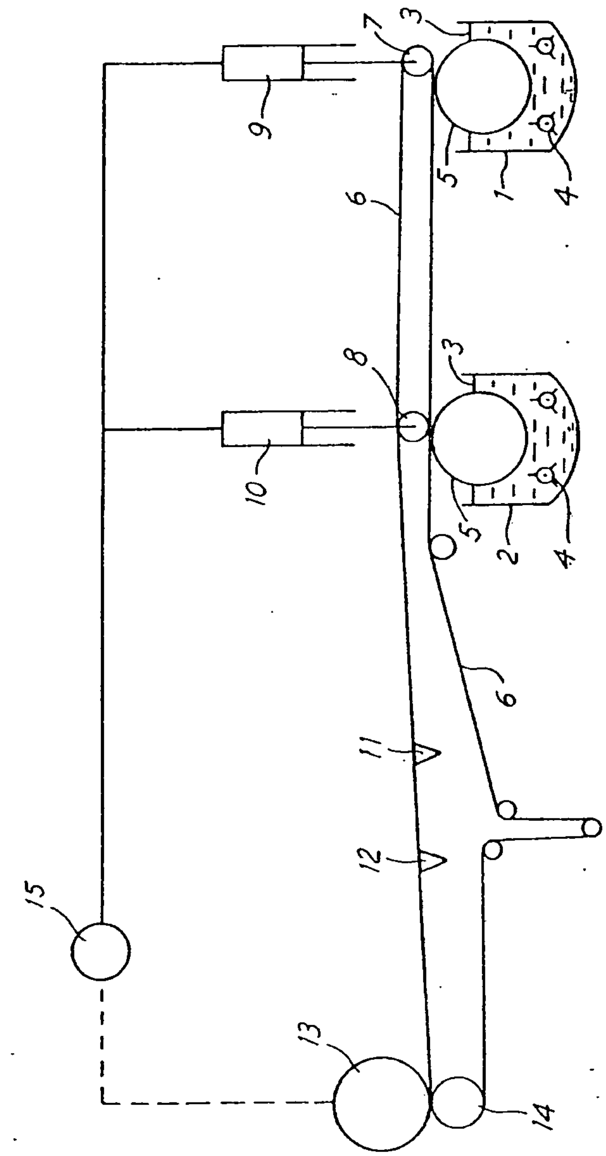
anschließendes Verfestigen des Bindemittels in der entwässerten Aufschlämmung, dadurch gekennzeichnet, daß der eingesetzte Ton ein plastischer Ton ist, der 5 bis 30 Gew.-% des Feststoffgehaltes der Aufschlämmung ausmacht und die Schrumpfung des Verbundmaterials während der Verfestigung des Bindemittels vermindert, und die Kohlefasern einen Zugmodul von nicht mehr als 125 GPa besitzen und 0,1 bis 2,5 Gew.-% des Feststoffgehalts der Aufschlämmung ausmachen.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der plastische Ton 10 bis 20 Gew.-% der Aufschlämmungsfeststoffe ausmacht.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Kohlefasern einen Zugmodul zwischen 10 und 100 GPa besitzen.

4. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Kohlefasern einen Zugmodul zwischen 15 und 80 GPa besitzen.

5. Verbundmaterial, erhalten nach dem Verfahren gemäß einem der vorhergehenden Ansprüche.



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